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Kinetics of zinc ions removal from effluents using ion exchange resin

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ABSTRACT

The ability of a new ion exchange resin to remove zinc ions from effluent has been studied. The equilibrium exchange capacity has been determined as 2.7 mmol/g resin and analysed using the Langmuir, Freundlich and Redlich–Peterson equations. The Redlich–Peterson gave the best-fit to the experimental data.

A series of kinetic studies were carried out in an agitated batch reactor. Three variables were studied, initial zinc ion concentration, resin mass and resin particle size. The results were analysed using three kinetic models, pseudo-first order, pseudo-second order and the Elovich model. The results were compared on the basis of SSE values and the best-fit correlation of the experimental data was obtained using the Elovich model which suggests a chemisorption process.

1. Introduction

Heavy metal ions are one of the major pollutants to human water resources. Most heavy metals are extremely toxic, non-biodegradable and tend to accumulate as metalloorganic complexes in living organisms.

Zinc is a raw material for corrosion-resistant alloys and brass, and for galvanizing steel and iron products. Zinc oxide is a white pigment for rubber and paper. On the other hand, zinc also is an essential element for human health life. It is one of the components of certain proteins inside the human body. Although zinc is a key element for humans, free zinc ion in solution is highly toxic to plants, invertebrates and even vertebrate fish. Trace amounts of free zinc ions can cause heavy damage to the environment and kill some organisms. Excessive intake of zinc can promote deficiency in other dietary minerals. The USEPA do not have enough data to evaluate the carcinogenicity of zinc and its compounds (USEPA [27]). According to Guidelines for Drinking Water Quality of the World Health Organisation (GDWQ-WHO), the daily requirement of zinc of an adult human is 15–22 mg/day (WHO [28]). The Institute of Medicine (IOM) recommended 40 mg/day as a tolerable upper intake level for adults from foods and supplements (Institute of Medicine [24]).

Chemical precipitation (Amrutech, KMT International Inc. [23]) has been conventionally used for metal ion removal, but this technique has difficulty in meeting the latest environmental standards [1] and it produces large amounts of sludge. Recently several studies on the removal of zinc from effluents using low-cost biosorbents have been reported [2–6]. In most cases, the zinc uptake capacities are quite low and the biosorbents are susceptible to degradation at low pH acid regeneration.

The most popular removal materials are ion exchangers/zeolites [7–9] whereby zinc can exchange preferentially with other ions, such as, H^+, Ca^{2+}, Na^+. Some biomaterials can also be utilised as removal materials [10–13].

In the present work a new ion exchanger, a sodium immidodiacetate has been tested for the removal of zinc ions. The resin capacity is compared to two commercially available resins and the kinetics of the zinc ions removal process are determined.

2. Experimental

2.1. Material in experiments

2.1.1. Ion exchange resin

An ion exchange resin is a synthetic organic material, its polymeric base usually is polystyrene. The resin used in experiments was supplied by a China company, the Suqing Group. A chelating resin (D401) was chosen in the experiments.

The behaviour of this chelating resin is similar to weak acid cation resins but it has high degree of selectivity for heavy metal cations. It forms stable complexes with the heavy metal ions. In fact, the functional group of this resin is iminodiacetate, as shown in Fig. 1.

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Nomenclature

a	Elovich equation constant (mmol/g min)
a_F	Freundlich isotherm constant
a_L	Langmuir isotherm constant (1/L mmol)
a_R	Redlich–Peterson isotherm constant ((1/L mmol)^{br})
b	Elovich equation constant (g/mmol)
b_F	Freundlich isotherm exponent
b_R	Redlich–Peterson isotherm exponent
C_e	metal ion concentration at equilibrium (M)
C_0	initial concentration of metal ion solution (M)
D	impeller diameter (m)
D_i	vessel inner diameter (m)
k_f	pseudo-first order equation rate constant (1/min)
k_s	pseudo-second order equation rate constant (g resin/mmol min)
K_L	Langmuir isotherm constant (L/g)
K_R	Redlich–Peterson isotherm constant (L/g)
m	mass of resin (g)
N_i	rotation speed of impeller (RPS)
N_p	power number
P	power consumption of the slurry (W)
q_{cal}	theoretical sorption capacity (mmol/g resin)
q_e	ion concentration on resin at equilibrium (mmol/g resin)
q_{exp}	experimental sorption capacity (mmol/g resin)
q_t	ion concentration on resin at specific time (mmol/g resin)
q_0	initial ion concentration on resin (mmol/g resin)
SSE	sum of the error squares
t	time (min)
t_0	Elovich equation time constant (min)
V	volume of metal ion solution (L)

Greek letters

$(\Phi_i)_o$	the total number of active sites on the sorbent surface
$(\Phi_i)_t$	the number of active sites occupied
ρ_l	density of liquid (kg/m^3)

Table 1 shows the physical and chemical properties data of D401 resin which is supplied by the supplier (Suqing Group [26]).

2.1.2. Adsorbates

Analytical-grade zinc chloride ($ZnCl_2$) was provided by BDH chemicals. Stock solutions of zinc metal ion were prepared using deionised (DI) water.

2.2. Experimental studies

2.2.1. Pre-treatment of resin

The chelating resin supplied was in the sodium form. However, the sodium content of the resin may not be consistent. Pre-treatment of resin, therefore, was required to ensure consistency of the experimental results and control the sodium content. The resins were immersed into 8% (w/w) hydrochloric acid with a portion 180 mL HCl/L resin more than 45 min to replace all the sodium ions by hydrogen ions, since the acid was in excess.

Then the resins were immersed into 4% (w/w) sodium hydroxide solution with a portion 60 g NaOH/L resin for more than 45 min to replace the hydrogen ions by sodium ions. The target sodium content of the resin should be 3 meq/g. The resins were then washed with DI water until the pH value of washing solution was below pH 11.

The resins were dried at 100–110 °C for at least 3 days and allowed to cool in a desiccator. Finally, the resins were sieved to separate the material into discrete particle size ranges, namely, 450–600 μm, 600–710 μm and 710–1000 μm particle size resins, which were then used in the experiments.

2.2.2. Agitation time for sorption isotherm studies

2.2.2.1. Methodology. The equilibrium time for the sorption isotherm needs to be identified before any other experiments are conducted. A fixed mass of 0.100 g resin was added to each polypropylene bottle. Then 50 mL of zinc metal ion solution was transferred into each bottle by using a pipette. The bottles were placed onto a shaker and the shaker speed was adjusted to provide an agitation speed of 200 rpm and to control the temperature at a constant (25 ± 2 °C). Each bottle was removed from the shaker at specified time and the zinc ion solution was collected into a sample tube. The initial and final concentrations of all the samples were determined by utilizing an inductively coupled plasma-atomic emission spectrophotometer (ICP-AES).

The equilibrium was reached after 72 h for the zinc ions. To ensure all isotherms achieved equilibrium, the experiment agitation time was defined as 96 h in all further isotherm experiments.

2.2.3. Equilibrium sorption isotherms

2.2.3.1. Methodology. A fixed mass of resin was weighed into 100 mL polypropylene bottles. The zinc ion solution was transfer red into each bottle by using pipette. Then 8% (w/w) hydrochloric acid was used to adjust the initial pH of the solution to the corresponding value. The bottles were placed onto a shaker with a speed of 200 rpm for 96 h to ensure equilibrium of each sample was reached. The initial and final concentrations of the samples

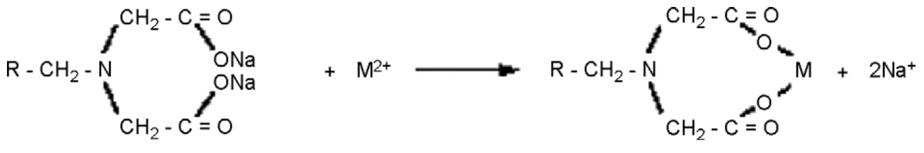

Fig. 1. Functional group of D401 resin (Purolite International [25]).

Table 1
Physical and chemical properties of D401 resin

	Ionic form	Total capacity min (mmol/mL)	Water retention (%)	Shipping weight (g/mL)	Specific density (g/mL)	Maximum reversible swelling	Remarks
D401	Na	0.6(Cu^{2+})	52–58	0.72–0.78	1.15–1.25	H → Na 40%	Macroporous iminodiacetate resin. Highly selective for multi-valence metals.

were determined by ICP-AES. The sorption capacity (q_e) of the resin could be calculated by the obtained data.

By the mass balance equation, the total number of moles of zinc ion in solution and resin is equal to the number of moles of ion adsorbed onto the resin plus the number of moles of zinc ion remaining in the final solution.

$$m(q_0 - q_e) = V(C_e - C_0) \quad (1)$$

When fresh resin is being used, $q_0 = 0$

Therefore,

$$q_e = \frac{V}{m}(C_0 - C_e) \quad (2)$$

where V = volume of zinc ion solution (L); m = mass of resin (g); C_0 = initial concentration of zinc ion solution (M); C_e = zinc ion concentration in solution at equilibrium (M); q_0 = initial zinc ion concentration on resin (mol/g resin); q_e = zinc ion concentration on resin at equilibrium (mol/g resin).

2.3. Batch contact time studies

Batch kinetic experiments are used to investigate the influence of different parameters on the adsorption rate. A standard configuration of adsorption vessel and stirrer was used in all of the experiments [14]. In the agitated batch adsorber the mixing was very vigorous due to the presence of a mechanical agitator and the kinetic experimental results showed that equilibrium capacity could be achieved in 600 min. In the equilibrium studies only a water bath shaker was used and the experiments took 720 min to reach equilibrium.

2.3.1. Installation of batch kinetic experiment vessel

The tank configuration was used to identify the relative dimensions of the vessel and mixing components [14]. The dimension of each component was derived by the inner diameter of the tank D_i (Fig. 2).

- Vessel inner diameter = D_i
- Height of baffle = 0.2 m
- Baffle width = 0.075D_i
- Height of liquid in the vessel = D_i
- Impeller diameter = 0.5D_i
- Width of the blade of impeller = 0.1D_i
- Distance from the vessel bottom to impeller blade = 0.5D_i

A 2 L plastic vessel was used as the adsorption tank with the inner diameter 0.13 m to hold 1.70 L metal ion solution for the kinetic experiment. A flat plastic impeller with six blades provided mixing effect to the solution. The diameter of the impeller was 0.065 m and the height of all the blades was 0.013 m. An overhead stirrer was used to driver the impeller using a 0.005 m diameter plastic shaft. Six plastic baffles were located around the circumference of the vessel with a position at 60° intervals and held securely in place on the top of the vessel. The baffles prevent the formation of a vortex and the consequential reduction in the relative motion between the solid and liquid. Each baffle was located slightly away from the wall of the vessel to prevent the solid accumulation. The alignment of the impeller could prevent the power loss due to air entrainment. The power number of this standard alignment vessel can be calculated by using Eq. (3) [14].

$$P = \rho_l \times N_P \times N_i^3 \times D^5 = 3.27\,\mathrm{W} \quad (3)$$

where P = power consumption of the slurry (W); ρ_l = density of liquid (kg/m^3); N_p = power number; N_i = rotation speed of impeller (rps); D = impeller diameter (m).

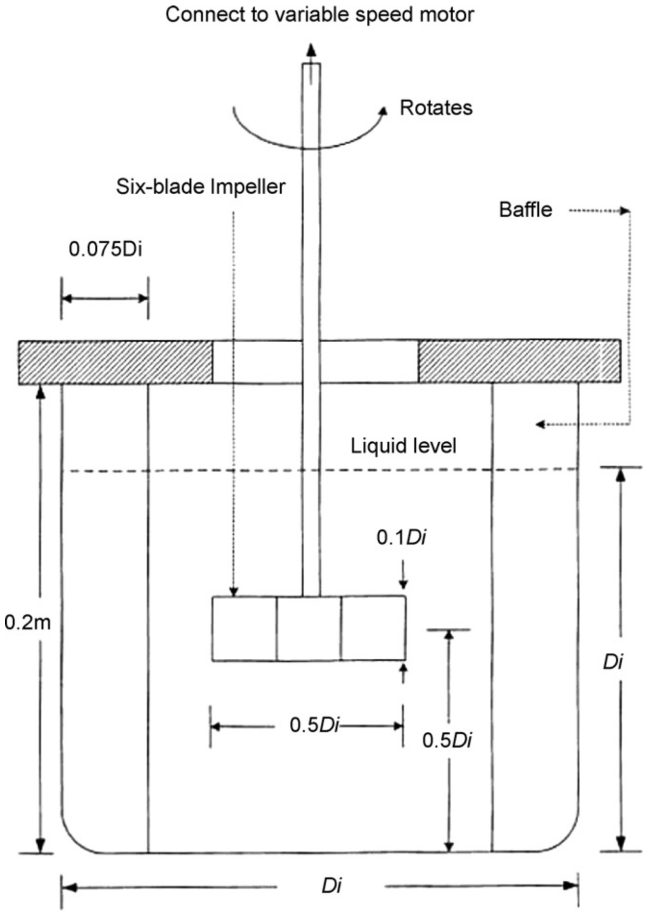

Fig. 2. Standard tank configuration for batch contact time studies.

On this basis the power number is 9.5

2.3.2. Identification of experimental parameters

The sorption process can be affected by different factors, such as mass of sorbent, initial concentration of liquid, resin particle size, pH value and agitation speed. Three different parameters have been investigated in the experiments, namely, initial zinc ion solution concentration, resin mass and resin particle size. The initial pH was fixed but the pH profile was measured throughout the batch kinetic experiments. A constant agitation speed of 400 rpm to obtain a “well-mixed” system. In previous studies [15], it has been shown for slow diffusional mass transport processes that the agitation influences the rate of external mass transfer across the boundary layer and increases the adsorption rate in the early stages of the mass transport process. In the present study, it can be seen from the batch kinetic figures that approximately 50% of the isotherm capacity uptake occurs in less than 1 h. On this basis, increasing the degree of agitation further will have little or no effect on enhancing the adsorption rate.

3. Theory of equilibrium isotherm models

The main purpose of the isotherm study is to identify the maximum capacity of each sorbent for different sorbates. The maximum capacity can be obtained from the experimental data of the equilibrium isotherm experiment. To determine the best-fit model for the sorption system, the results are substituted into the equilibrium isotherm model equations.

3.1. The Langmuir equation

In 1918, Langmuir [16] developed a theoretical equilibrium isotherm to calculate the amount of gas adsorbed onto a surface to the pressure of the gas. This model is a well-known isotherm model and widely used in sorption systems. It is suitable for describing numerous homogeneous, constant energy solution sorption systems.

The mathematical expression for the Langmuir equation is:

$$q_\mathrm{e} = \frac{K_\mathrm{L} C_\mathrm{e}}{1 + a_\mathrm{L} C_\mathrm{e}} \tag{4}$$

3.2. The Freundlich equation

In 1906, Freundlich [17] developed the earliest recognized sorption isotherm modelling equation. It can apply to nonideal sorption onto heterogeneous surfaces and multilayer sorption of the sorbate.

The mathematical expression for the Freundlich equation:

$$q_\mathrm{e} = a_\mathrm{F} C_\mathrm{e}^{\mathrm{b_F}} \tag{5}$$

3.3. The Redlich–Peterson equation

The Redlich–Peterson equation incorporates with the features of the Langmuir and Freundlich equation. In 1978, Jossens et al. [18] modified the three parameter isotherm first proposed by Redlich and Peterson and developed the well-established Redlich–Peterson isotherm.

The mathematical expression of the Redlich–Peterson equation:

$$q_\mathrm{e} = \frac{K_\mathrm{R} C_\mathrm{e}}{1 + a_\mathrm{R} C_\mathrm{e}^{\mathrm{b_R}}} \tag{6}$$

4. Theory of pseudo-kinetic models

Sorption kinetic mechanisms can be based on diffusion mass transfer processes or chemical reaction kinetics. The sorption kinetics of a sorbent depends on the property of the sorbate, experimental conditions, temperature and pH value. Each combination of sorbent and sorbate has a unique metal ion–sorbent interaction. The sorption process can be a reaction kinetic process, mass transfer process or a combination of the two different processes.

In this study, the main focus is based on the analysis of the reaction kinetics of the sorption process. Three different reaction kinetic models (pseudo-first order equation, pseudo-second order equation and Elovich equation were applied to determine the reaction order and rate constant of the ion exchange between the resin and zinc ion in solution.

4.1. The pseudo-first order equation

The pseudo-first order reaction equation for solid–liquid sorption system was proposed by Lagergren in 1898 [19]. This equation has been traditionally the most conventional model used model and often used for liquid sorption modelling.

The general mathematical expression is:

$$\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = k_\mathrm{f}(q_\mathrm{e} - q_\mathrm{t}) \tag{7}$$

Integrating Eq. (7) with the following boundary conditions:

(1) $t = 0, q_\mathrm{t} = 0$
(2) $t = t, q_\mathrm{t} = q_\mathrm{t}$

Therefore,

$$q_\mathrm{t} = q_\mathrm{e}(1 - \exp(-k_\mathrm{f} t)) \tag{8}$$

The pseudo-first order reaction is generally most suitable to the early stages of a sorption process, typically up to 20% uptake. After this the high surface loading, the significant change in the liquid phase zinc ion concentration and the large reduction in resin sites now available for adsorption, tend to make the model less applicable at higher loadings. Therefore, the next two kinetic models have been developed and applied.

4.2. The pseudo-second order equation

More recently, Ho and McKay [20,21] proposed a second order equation based on the amount of sorbate which was sorbed onto the sorbent. The second order equation can be derived from chemical equations.

The general mathematical expression is:

$$\frac{\mathrm{d}(\Phi)_\mathrm{t}}{\mathrm{d}t} = k_\Phi[(\Phi_i)_0 - (\Phi_i)_\mathrm{t}]^2 \tag{9}$$

where, $i = 1, 2$; $(\Phi_i)_\mathrm{o}$: the total number of active sites on the sorbent surface; $(\Phi_i)_\mathrm{t}$: the number of active sites occupied.

In terms of solid phase concentration, Eq. (9) becomes:

$$\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = k_\mathrm{s}[q_\mathrm{e} - q_\mathrm{t}]^2 \tag{10}$$

Integrating Eq. (10) with following boundary conditions:

(1) $t = 0, q_\mathrm{t} = 0$
(2) $t = t, q_\mathrm{t} = q_\mathrm{t}$

Therefore,

$$q_\mathrm{t} = \frac{k_\mathrm{s} q_\mathrm{e}^2 t}{1 + k_\mathrm{s} q_\mathrm{e} t} \tag{11}$$

4.3. The Elovich equation

The Elovich equation, generally, is applied to chemisorption kinetic analysis. In 1960, Low [22] made a detail investigation of the use of the Elovich equation in the kinetic analysis of the chemisorption of gases onto a solid phase.

The mathematical expression is:

$$\frac{\mathrm{d}q_\mathrm{t}}{\mathrm{d}t} = a\exp(-bq_\mathrm{t}) \tag{12}$$

Integrating Eq. (12) with the following boundary conditions:

(1) $t = 0, q_\mathrm{t} = 0$
(2) $t = t, q_\mathrm{t} = q_\mathrm{t}$

Therefore,

$$q_\mathrm{t} = \frac{1}{b}\ln(1 + abt) \tag{13}$$

Let $t_0 = (1/ab)$, and expand Eq. (13);

$$q_\mathrm{t} = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t + t_0) \tag{14}$$

The time constant, t_0, is a compensating factor for certain circumstances, for instance, resin with some pre-loading, or an initial rapid surface reaction on active sites or an initial external film mass transfer.

5. Theory of pseudo-kinetic models

5.1. Equilibrium isotherms

The experimental data of the zinc system equilibrium isotherm, were compared using the Langmuir, Freundlich and Redlich–Peterson isotherm equations. The experimental results are

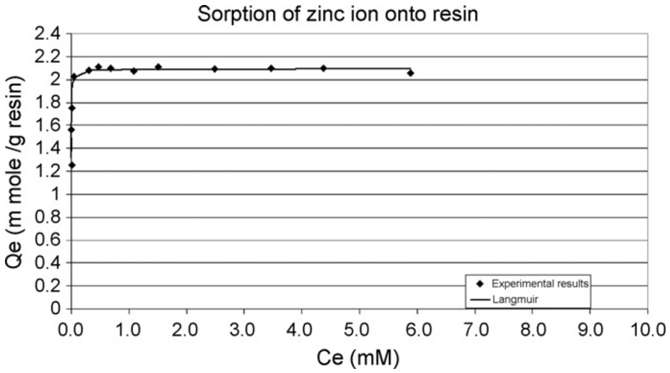

Fig. 3. Sorption of zinc ion onto resin D401.

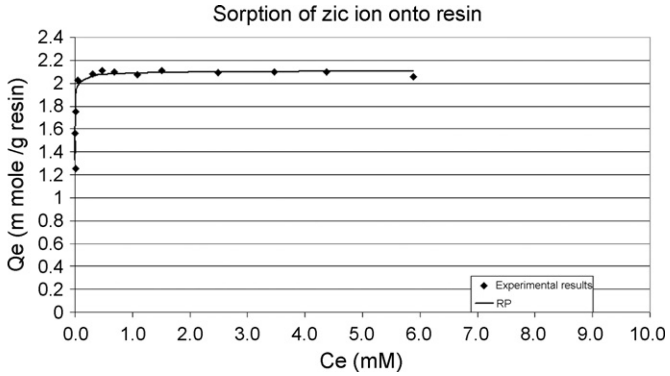

Fig. 4. Sorption of zinc ion onto resin D401.

shown in Figs. 3 and 4 and exhibit a rectangular isotherm characteristic. All the parameters of each model were determined by a built-in function of Microsoft Office "Excel" program. The isotherm constants are presented in Table 2.

The equilibrium isotherm results were input into the Excel spreadsheet and the parameters of each isotherm were calculated by the modelling equations by minimizing the difference between the experimental data and the theoretically predicted models data. The sum of the error squares (SSE) method was the objective function to obtain those parameters.

$$\mathrm{SSE} = \sum (q_{\exp} - q_{\mathrm{cal}})^2 \tag{15}$$

The experimental sorption capacity ($q_{\exp}$) can be obtained by the mass balance Eq. (2). The theoretical sorption capacity (q_{cal}) is determined for the each isotherm model. The parameters of each isotherm equation can be determined by minimizing the SSE. The best-fit model should have the least SSE value; therefore, this model can be obtained by comparing the SSE of each model. The SSE values are compared in Table 3.

By comparing the SSE of different models in the three isotherm systems, it seems that Redlich–Peterson isotherm was the best-fit although the SSE for the Redlich–Peterson and the Langmuir are very similar. The quality of the fit of the Langmuir isotherm, a two-parameter equation, can be emphasized since the Redlich – Peterson is a three-parameter equation. Furthermore, the value of the Redlich–Peterson exponent, b_R, is 0.99 when the exponent is unity, this three-parameter equation reduces to the Langmuir. Since the ion exchanger D401 is a new material, zinc isotherms for other commercial resins were determined and compared on a capacity versus cost basis in Table 4.

Table 3
The SSE of different isotherm equations

Metal ion	Langmuir	Freundlich	Redlich–Peterson
Zinc	0.1166	0.2806	0.1151

It can be concluded that the capacity of D401 is of a comparable magnitude. Although D401 has the lowest capacity, however, on a relative cost comparison basis, to remove 1 mol of zinc ions the relative costs are $US 74.02 for D401, $US 204.00 for S930 and $US 114.40 for TP207.

5.2. *Batch kinetic systems*

The batch sorption system is a well-developed system for application in the field of water pollution collected in small scale plants. The suitability of a sorbent is determined by the cost, sorption performance and regeneration efficiency. In this research, the main target was to investigate the sorption performance of resin for zinc metal ions.

Two important parameters govern the sorption performance of a batch system, namely, the sorption equilibrium and the sorption rate which controls the performance of a batch system by determining the residence time required to achieve a fixed percentage removal of the zinc ions. The rate of a sorption process affects the designed contact time of the batch system. It may be the case that a sorbent may have a large sorption capacity for a sorbate but it has a very low sorption rate. Obviously, an ideal sorbent for a batch system should have a large sorption capacity and fast removal rate for a particular sorbate.

The batch kinetic experimental data was substituted into an Excel spreadsheet to identify the most suitable kinetic model. Three types of sorption kinetic models were utilised for the sorption of metal ions onto resin. The pseudo-first order equation, the pseudo-second order equation and the Elovich equation were the three types of kinetic models.

In a similar analytical-procedure as the approach for recognizing the best-fit isotherm model, the specific parameters of each kinetic model were determined by minimizing the SSE. Then, by comparing the SSE of the models, the best-fit model was obtained.

5.2.1. *The pseudo-first order equation*

The pseudo-first order equation has one changing parameter, k_f, and the q_e was obtained from the isotherm equation. In the Excel program, a built-in function "Solver" was used to minimize the difference between experimental data and the theoretical values. The best-fit rate parameters, k_f, for the pseudo-first order reaction are shown in Table 5, for the three process parameters, initial zinc ion concentration, resin mass and resin particle size.

Figs. 5 and 6 show the theoretical pseudo-first order plots at initial concentration values of 1.7 mM and 2.3 mM. Figs. 7 and 8

Table 2
Isotherm Constants for Zinc Ions on D401 Resin

Langmuir constants		Freundlich constants		Redlich–Peterson constants	
K_L (L/g)	871	a_F	2.041	a_R $(1/\mathrm{L\,mmol})^{br}$	447
a_L (1/L mmol)	417	b_F	0.045	b_R	0.995
				K_R (L/g)	933

Table 4
Comparison of zinc ion capacities on various resins

Product	Type	Ionic form	Size (mm)	Total capacity (meq/mL)	Remark
LSC-100	Iminodiacetate	Na^+	0.315–1.25	1.3	Chelating resin specific for heavy metal removal
D401	Macroporous polystyrene chelating iminodiacetate	Na^+	0.4–1.25	2.1	Macroporous iminodiacetate resin. Highly selective for multi-valence metal ions. For separation of heavy and scarce metals.
TP207	Macroporous chelating iminodiacetate	Na^+	0.9	2.2	None
S930	Macroporous polystyrene	Na^+	0.3–1	0.94 (Na^+ form)	None

Table 5
Pseudo-first order rate parameters

	Zn concentration (mM)				
	1.7	2.0	2.3	2.6	2.9
k_f (L/min)	0.0100	0.0103	0.0116	0.0124	0.0132
	Resin mass (g)				
	0.9	1.1	1.3	1.5	1.7
k_f (L/min)	0.0167	0.0103	0.0075	0.0055	0.0043
	Resin dp (μm)				
	450–600	600–710	710–1000		
k_f (L/min)	0.0313	0.0068	0.0139		

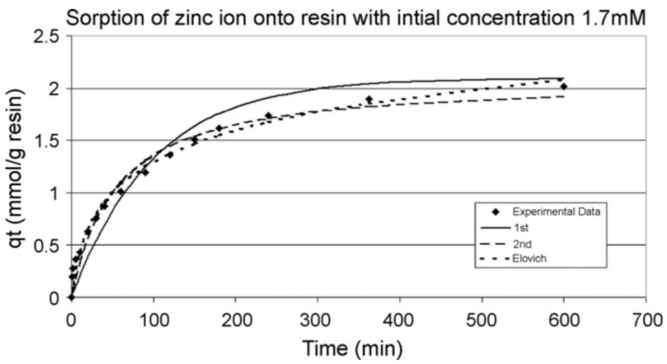

Fig. 5. Modelling of sorption of zinc onto resin with initial concentration 1.7 mM.

show the theoretical pseudo-first order plots at resin masses of 0.9 g and 1.7 g. Figs. 9 and 10 show the theoretical pseudo-first order plots of concentration versus time for 450–600 μm and 710–1000 μm.

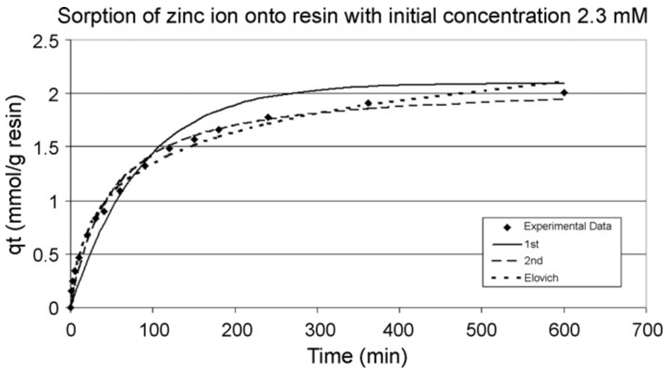

Fig. 6. Modelling of sorption of zinc onto resin with initial concentration 2.3 mM.

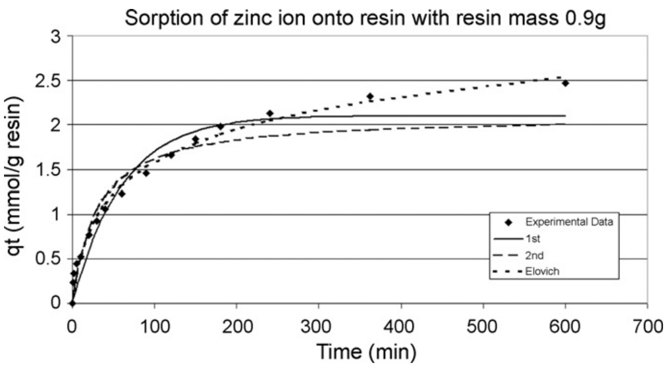

Fig. 7. Modelling of sorption of zinc onto resin with resin mass 0.9 g.

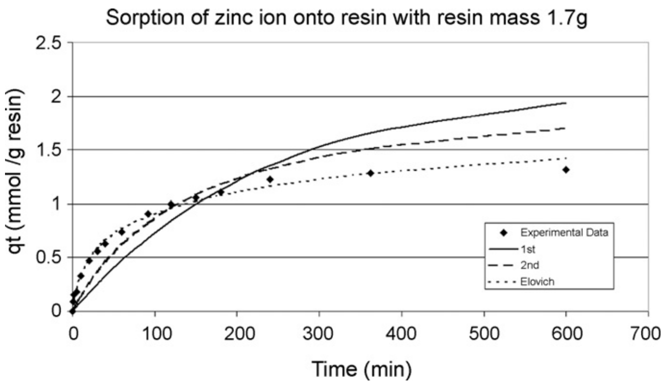

Fig. 8. Modelling of sorption of zinc onto resin with resin mass 1.7 g.

5.2.2. The pseudo-second order equation

Eq. (11) shows the mathematical expression of the pseudo-second order equation. The rate constant of this equation is k_s and it is the changing variable for minimizing the SSE. The values of

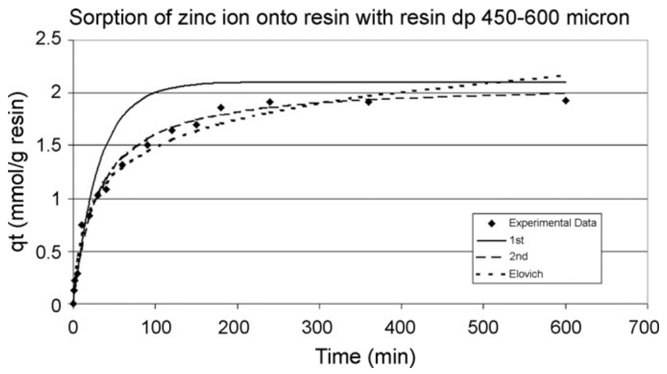

Fig. 9. Modelling of sorption of zinc onto resin with resin dp 450–600 μm.

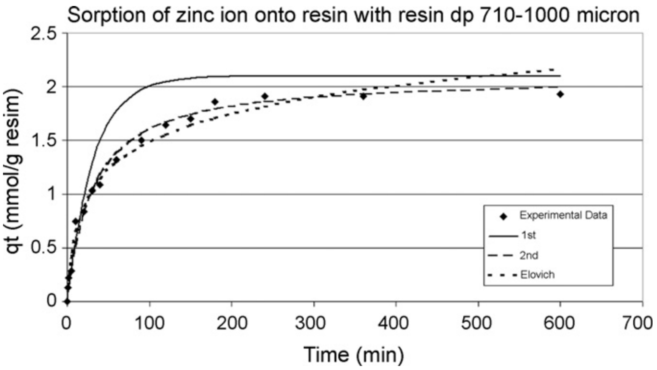

Fig. 10. Modelling of sorption of zinc onto resin with resin dp 710–1000 μm.

Table 6
Pseudo-second order rate parameters

	Zn concentration (mM)				
	1.7	2.0	2.3	2.6	2.9
k_S (g/mmol min)	0.0087	0.0088	0.0101	0.0108	0.0116
	Resin mass (g)				
	0.9	1.1	1.3	1.5	1.7
k_S (g/mmol min)	0.0159	0.0088	0.0062	0.0044	0.0034
	Resin dp (μm)				
	450–600	600–710	710–1000		
k_S (g/mmol min)	0.0154	0.0054	0.0126		

k_S for the three process variables are shown in Table 6. The resin masses, initial zinc ion concentrations and resin particle sizes used throughout the batch kinetic studies are shown in this table. The equilibrium capacity, q_e, is 2.1 mmol zinc/g resin.

The pseudo-second plots are shown in Figs. 5–10 for the three process variables.

5.2.3. *Elovich equation*

The Elovich equation contains two variables a and b and it is an empirical equation which is independent from the q_e of the isotherm experimental results. Eqs. (13) and (14) are the mathematical expression of the Elovich equation. The time constant t_0 is equal to $(ab)^{-1}$. By changing the parameters a and b, the minimum SSE can be obtained. The values of the constants a and b are presented in Table 7. The plots of the Elovich equation are shown in Figs. 5–10.

Table 7
Elovich equation constants

	1.7 mM	2.0 mM	2.3 mM	2.6 mM	2.9 mM
a	0.0747	0.0675	0.0907	0.0902	0.0985
b	2.2138	2.1059	2.2863	2.2164	2.2261
	0.9 g	1.1 g	1.3 g	1.5 g	1.7 g
a	0.0913	0.0675	0.0767	0.0662	0.0637
b	1.8113	2.1059	2.7020	3.0224	3.4403
	450–600 μm	600–710 μm	710–1000 μm		
a	0.1748	0.0470	0.1592		
b	2.5822	2.2678	2.6304		

Unit: a: mmol/g min: b: g/mmol.

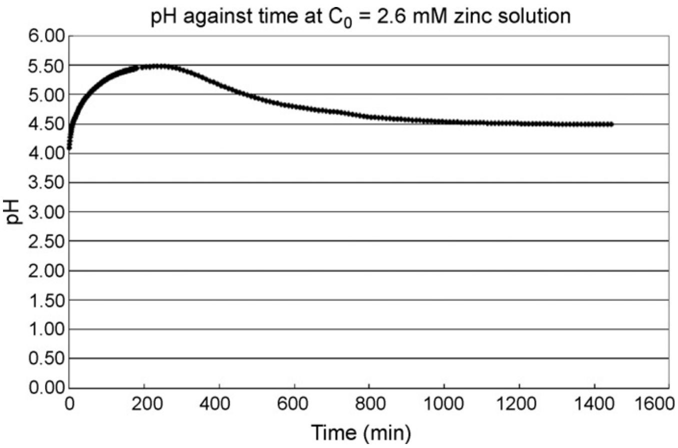

Fig. 11. pH variation against time at $C_0 = 2.6$ mM zinc solution.

Table 8
The SSE of each kinetic models of initial concentration effect of zinc system

Zn conc. (mM)	Pseudo-first order	Pseudo-second order	Elovich
1.7	0.4536	0.1605	0.0747
2.0	0.3212	0.0599	0.0482
2.3	0.4213	0.0880	0.0479
2.6	0.3448	0.0491	0.0420
2.9	0.3448	0.0826	0.0658

5.2.4. *Mechanism and pH profile*

The main mechanism of the ion exchange process of zinc ions on D401 resin is shown in Fig. 1. However, another much slower exchange process also takes place. The pH versus time profile is shown in Fig. 11. The solution pH rises from the initial value of 4.0 to a value of 5.5 during the Zn–Na exchange, then pH falls to a final value of 4.50 due to Zn–H ion exchange. The Na–Zn exchange begins to slow after approximately 250 min. Then the pH starts to decrease. At this point most of the sodium ions have exchanged but there is now a longer, slower process of exchange between Zn^{2+} and the residual resin H^+ ions. On the batch kinetic model curves often the last one or two experimental points fall below the Elovich theoretical plot, based on the much faster sodium exchange process.

5.2.5. *Kinetic model selection*

The rate constants and other parameters of the three different batch kinetic equations were obtained by minimizing SSE by using the Excel spreadsheet program by iteration. Three different operating parameters were investigated in this research. Table 8 shows the initial concentration effect of the zinc metal ion to the kinetic models.

The effects of C_0, resin mass and resin dp are compared in Tables 8–10, respectively and in all cases the Elovich model has the smallest SSE values.

Table 9
The SSE of each kinetic models of sorbent mass effect of zinc system

Resin mass (g)	Pseudo-first order	Pseudo-second order	Elovich
0.9	0.5349	0.6431	0.1115
1.1	0.3212	0.0599	0.0482
1.3	0.7428	0.1729	0.0343
1.5	0.9364	0.2843	0.0226
1.7	1.0660	0.4121	0.0276

Table 10
The SSE of each kinetic models with particle size range

dp (μm)	Pseudo-first order	Pseudo-second order	Elovich
450–600	1.2018	0.1025	0.1560
600–710	0.4970	0.0897	0.0627
710–1000	0.6882	0.2273	0.0779

6. Conclusion

In order to determine the most appropriate adsorption isotherm of the resin D401, the experimental data were substituted to three isotherm models, Langmuir, Freundlich and Redlich–Peterson. The isotherm parameters and the best-fit model equation were identified based on the least value of sum of error squares. The Redlich–Peterson model can be used to best describe the sorption isotherm of zinc metal ions onto resin.

In terms of the sorption kinetic experiments, the results of three sorption parameter systems were substituted to three kinetic models which were the pseudo-first order, pseudo-second order and Elovich equation. The sorption kinetics of zinc metal ions onto resin can be best described by the Elovich equation, the most applicable model for this chemisorption ion-exchange mechanism process.

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